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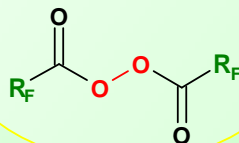
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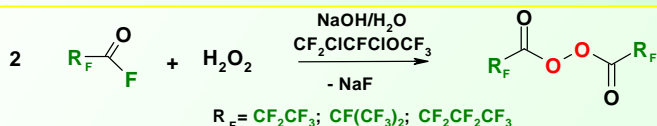
Fluorinated peroxides exhibits different chemical reactivities compared to the corresponding hydrogenated peroxides, in particular decomposition behaviors.

## PERFLUORODIACYL PEROXIDES

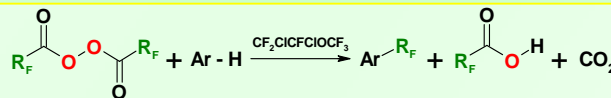


The presence of fluoroalkyl groups, that are strong electron-withdrawing moieties, can greatly weaken the O-O bond in addition to lowering the energy level of the antibonding O-O bond, if compared to the corresponding non-fluorinated peroxides.

## SYNTHESIS

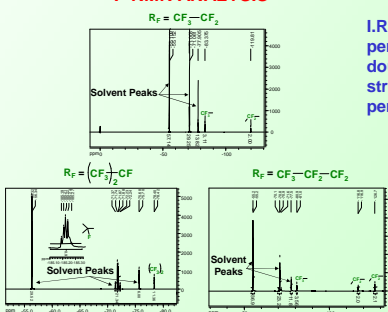


## PERFLUOROALKYLATION OF AROMATIC SUBSTRATES



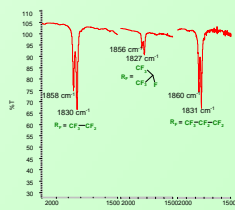
## CHARACTERIZATION

### <sup>19</sup>F-NMR ANALYSIS



### I.R. ANALYSIS

I.R. analysis confirms the synthesis of diacyl peroxides: the spectra show the typical double signals (1850 and 1830 cm<sup>-1</sup>) due to stretchings of non-symmetrical carbonyl into peroxydiacyl function.



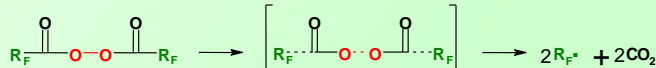
Alkylated structures of the products are determined by <sup>19</sup>F-NMR, GC and MS-GC analyses. On substrates with available benzylic position the presence of the corresponding by-products has been verified. The typical peaks of R<sub>F</sub>COOH, as reaction evidence, have been also confirmed.

Ar-H	Products	Yields		
		R <sub>F</sub> = CF <sub>2</sub> CF <sub>3</sub>	R <sub>F</sub> = CF(CF <sub>3</sub> ) <sub>2</sub>	R <sub>F</sub> = CF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>
		95%	97%	86%
		89% (4%) <sup>a</sup>	69% (31%) <sup>a</sup>	96% (4%) <sup>a</sup>
		39%	68%	64%

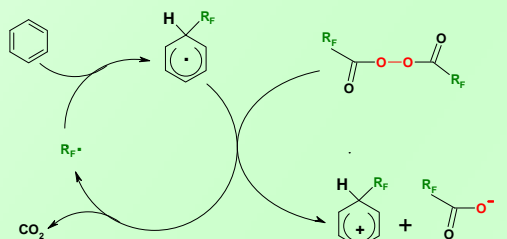
<sup>a</sup> Yields of benzylic byproducts.

## RADICAL CHAIN MECHANISM

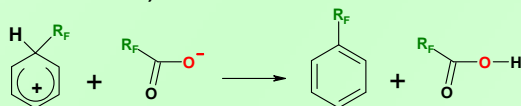
### 1) Thermolytic initiation



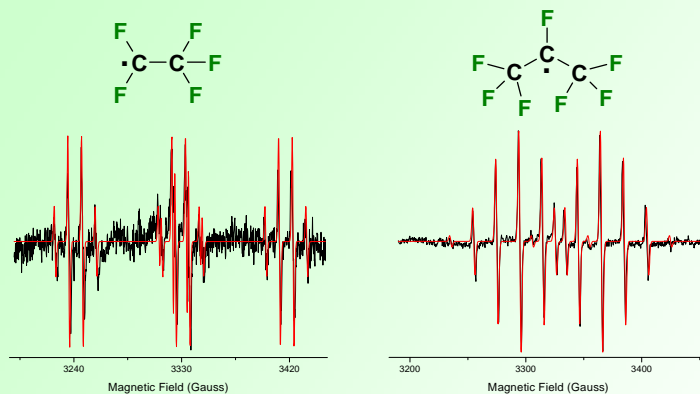
### 2) Electron-transfer propagation



### 3) Carbocation Aromatization



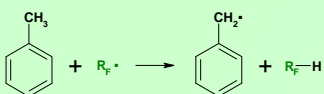
## DIACYL PEROXIDES AS FREE RADICAL SOURCES



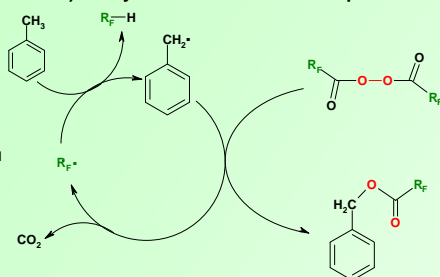
The EPR analyses confirm a stationary concentration of perfluorinated free radicals, obtained by the thermal decomposition of peroxides in perfluorinated solvent.

## BENZYLIC OXIDATION SIDE REACTION

### 1) Hydrogen Abstraction



### 2) Benzyl Radical Induced Decomposition



## CONCLUSIONS

- One procedure for the synthesis and the use of diacyl peroxides as reagents for perfluoroalkylation of electron-rich and electron-poor aromatic compounds has been developed.
- Reaction mechanism which comprehends a thermolytic initiation, successive propagation with electronic transfer reaction, hydrogen abstraction and radical induced decomposition has been proposed.
- Further information about the alkylation reaction will be obtained by the alkylation of suitable aromatic substrates and through the observation of free radical species formed in the reaction media.

## ACKNOWLEDGMENTS

Politecnico di Milano: Prof. G. Resnati; Dr. F. Meyer; Dr. R. Liantonio; Dr. Y. Carcenac; Dr. F. Chau; Mr. M. Ursini;  
 Università degli Studi di Padova: Prof. C. Corvaja; Dr. L. Franco;  
 Solvay-Solexis S.p.a.: Dr. I. Wlascics; Dr. M. Galimberti; Dr. E. Barchesi; Dr. S. Radice.